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(54) ELECTROMAGNETIC WAVE SHIELDING MATERIAL AND ITS MOLDING**(57)Abstract:**

PROBLEM TO BE SOLVED: To provide an electromagnetic wave shielding material exhibiting excellent electromagnetic wave shielding performance for protecting an apparatus against trouble due to electromagnetic wave especially in the high frequency region, and its molding.

SOLUTION: The electromagnetic wave shielding material is composed of a thermoplastic resin material containing specified quantity of carbon nanotube and conductive fibers. Its molding is also provided.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention]This invention relates to the thermoplastic resin composition which has electromagnetic wave shielding [outstanding]. the charge of a shield material used in more detail in fields, such as a personal digital assistant, electrical machinery electronic equipment, a household appliance article, a precision mechanical equipment, medical equipment, and electronic equipment for vehicles, in order to prevent the obstacle by an electric wave -- and -- and it is related with the becoming shielding member.

[0002]

[Description of the Prior Art]In the modern society by which computerization is advanced, from the necessity for efficient transfer of information, the mainstream of processing of information shifts to a digital system from an analog form, and a digital system is being established nowadays. In information processing by this digital system, for the purpose of the densification of the further information, high-frequency-ization of an electronic circuit etc. is advanced and more advanced computerization is attained.

[0003]Generally, since the signal level which generates a noise by the clock frequency used, but on the other hand is used is low, it is easy to be influenced by a foreign electromagnetic wave noise in a digital circuit. For this reason, it can be said that the electronic equipment using a digital circuit has a possibility that an electromagnetic wave noise will cause malfunction easily.

[0004]Since it is above, in the apparatus having an electric electronic component, the measure of making it not take out an electromagnetic wave noise and not influenced [both] by a foreign electromagnetic wave noise is demanded. Although the measure on an electronic circuit is also required about the measure against an electromagnetic wave noise, there are many views of shielding electromagnetic waves with a case, a shield plate, etc. which store an electric electronic component.

[0005]As the main art, the method of using conductive resin as a shield material, the method of performing metal plating, metal deposition, electric conduction paint, etc. to a resin production form, etc. are proposed.

[0006]However, although the method of shielding with the above-mentioned conductive resin is the method of mixing and fabricating conductive substances, such as carbon fiber and a metal fiber, to resin, since a conductive substance is covered by resin of an insulator, sufficient conductivity is not obtained. Although how to add a conductive substance so much or lengthen fiber length of carbon fiber etc. are considered that I will obtain sufficient conductivity, when electromagnetic wave shielding [more advanced] is required, still sufficient improvement effect is not accepted by these methods, either.

[0007]According to the method of giving metal plating, metal deposition, conductive coating material, etc. to a resin production form, the outstanding shielding effect is acquired, but. Since the shielding

effect which should be satisfied unless sufficient thickness is formed is not acquired, therefore floor to floor time becomes long or a process of operation increases, workability, process cost, etc. pose a problem. In the low frequency region, even if sufficient effect is seen, if it becomes a high frequency region near 800 MHz, it also has the character in which a shielding characteristic falls.

[0008]

[Problem(s) to be Solved by the Invention]The purpose of this invention solves the conventional problem mentioned above, has electromagnetic wave shielding [which excelled for preventing the obstacle of the apparatus by electromagnetic waves], and there is in providing the Plastic solid which consists of electro-magnetic interference sealed materials which consist of a thermoplastic resin composition excellent in especially the shield nature of a high frequency region, and it.

[0009]

[Means for Solving the Problem]To achieve the above objects, electro-magnetic interference sealed materials of this invention consist of a thermoplastic resin composition containing 0.5 to 20 % of the weight of carbon nanotubes, and 5 to 50 % of the weight of conductive fibers.

[0010]In electro-magnetic interference sealed materials of this invention, When said charge of a shield material is used as 1-mm-thick tabular mold goods, it is mentioned as desirable conditions that a field intensity shield level in frequency of 800 MHz which used and searched for the KEC method is less than -30dB, and that said conductive fiber is [each of] carbon fiber.

[0011]A Plastic solid of this invention consists of the above-mentioned electro-magnetic interference sealed materials.

[0012]

[Embodiment of the Invention]This invention is explained in full detail below.

[0013]There is no restriction in particular in the thermoplastics used in this invention, and specifically, Olefin system resin, such as polyethylene, polypropylene, polystyrene, ethylene / alpha olefin copolymer, Syndiotactic polystyrene, an AS resin (AKURIRO 2 tolyl / styrene copolymer), ABS plastics (acrylonitrile / styrene / butadiene copolymer), Aliphatic series system polyamide and these copolymers, such as styrene resin, such as HIPS (high impact polystyrene), nylon 6, Nylon 66, Nylon 610, Nylon 612, Nylon 11, and Nylon 12, 6T/66, 6T/6, 6T/12, 6T/610, 6I/66, 6T/6I, 6 T-systems, such as 6T/6I/66, or 6I system -- a copolymer (6T a hexamethylene terephthalate unit) Nylon system resin, like 6I expresses a hexamethylene isophthalate unit, Polyethylene terephthalate, polybutylene terephthalate, the polyethylene 2, 6-naphthalate, Non-liquid-crystal-polyester system resin, such as polybutylene 2,6-naphthalate, PORIE ylene isophthalate, and polybutylene isophthalate, and these copolymers, liquid crystal polyester, The polyarylene sulfide represented by the polyphenylene sulfide, Although polycarbonate, polysulfone, polyether sulphone, polyether imide, polyamidoimide, polyether ketone, a polyether ether ketone, polyacetal (a homopolymer, a copolymer), etc. are mentioned, Polyethylene which is excellent in mobility in making light-gage mold goods profitably like especially, Polypropylene, nylon 6, Nylon 66, 6T/66, 6T/6, 6T/6I, Crystalline thermoplastics, such as 6T/6I/66, polyethylene terephthalate, polybutylene terephthalate, liquid crystal polyester, a polyphenylene sulfide, and polyacetal (a homopolymer, a copolymer), is used preferably.

[0014]The carbon nanotube used by this invention is the material in which the layer structures which the carbon hex-steel side closed cylindrical, or such cylinder structures had multilayer structure arranged at nesting form. Even if the carbon nanotube comprises only layer structure, it may comprise only multilayer structure, and even if layer structure and multilayer structure are intermingled, it is not cared about. The carbon material which has the structure of a carbon nanotube selectively can also be used. It may be called by a name called a graphite fibril nanotube besides a name called a carbon nanotube.

[0015]A carbon nanotube generates arc discharge, for example between carbon electrodes, It can manufacture using heating, the method of making it sublimate, and a transition metal system catalyst by the method of carbonizing hydrocarbon by the gaseous phase under reducing

atmosphere, etc. by irradiating with a laser beam the method and silicon carbide which are grown up into the cathode surface of an electrode pattern. Anything of a gestalt can be used although the size and the gestalt of a carbon nanotube which are acquired by the difference in a manufacturing method change.

[0016]As for the loadings of the carbon nanotube in this invention, it is preferred that it is the viewpoint of the mobility at the time of shaping, the specific gravity of the mold goods obtained and intensity, and shield nature to 0.5 to 20% of the weight of the whole thermoplastic resin composition. It is 1 to 15 % of the weight more preferably.

[0017]If it is textiles which have conductivity as a conductive fiber used in this invention, there will be no restrictions in particular, and the textiles etc. which plated metal to metal fibers, such as copper, nickel, and silver, carbon fiber, and glass fiber and carbon fiber are mentioned. Especially, carbon fiber is preferably used in that it excels in the ease of getting used with a carbon nanotube.

[0018]The pitch based carbon fiber which restrictions in particular do not have in the carbon fiber used by this invention, and uses as a raw material the pitch which is the residue at the time of oil refining. And it is possible to use the polyacrylonitrile (PAN) system carbon fiber etc. which use poly acrylic fibers as a raw material, and 0.5–15 micrometers in diameter and tensile strength are mentioned for a fiber diameter as what has 1 – 7GPa and a modulus of elasticity in tension suitable [the carbon fiber of 40 – 400GPa].

[0019]From the field of the appearance of a mechanical physical property, a moldability, and a molded body surface, the loadings of the conductive fiber in the thermoplastic resin composition in this invention are 5 to 50% of the weight of the whole thermoplastic resin composition, and are 10 to 40 % of the weight preferably. Since the surface appearance of a moldability (mobility) not only worsening but a Plastic solid will also get worse if too large [if there are too few electric conduction textiles, the shielding characteristic and mechanical physical property of sufficient electromagnetic waves will not be acquired, but], it is not desirable.

[0020]The relation (L_w/d) between the weighted mean fiber length (L_w) of the electric conduction textiles which exist in this invention in the electromagnetic wave shielding member which consists of thermoplastic resin compositions, and the path (d) of these electric conduction textiles, It is desirable still more preferred that it is 10–150, and it is recommended in respect of the appearance of mechanical properties, conductivity, a moldability, and a molded body surface 15–100, and that it is 20–75 especially preferably.

[0021]The electric conduction fiber length and the fiber diameter of an electromagnetic wave shielding member which consist of thermoplastic resin compositions can be measured by microscope observation about 1000 arbitrary electric conduction textiles from the ash which burned the Plastic solid under 500 °C 5-hour argon gas atmosphere, and remained. The weighted mean fiber length (L_w) of textiles is expressed with a following formula (1).

Weighted mean fiber length (L_w) = $\frac{\sum (r_i \cdot L_i^2 \cdot L_i)}{\sum (r_i \cdot L_i^2)}$ (1)

However, density r of rho:electric-conduction textiles: The length of the electric conduction textiles of eye radius L_i : watch of electric conduction textiles.

[0022]To the thermoplastic resin composition which constitutes the electromagnetic wave shielding member of this invention. In the range which does not spoil a mechanical physical property, a moldability, surface appearance, etc., an antioxidant, The modifier of thermoplastics, such as a heat-resistant agent and fire retardant, and glass fiber, titanate acid KARIWISUKA, A zinc oxide whisker, a boric acid aluminum whisker, an aramid fiber, an alumina fiber, Fibrous fillers, such as silicon carbide fiber, ceramic fiber, an asbestos fiber, stone Coe textiles, and a metal fiber, Huaras Tena Ito, zeolite, a sericite, kaolin, talc, mica, Silicate, such as clay, pyrophyllite, bentonite, asbestos, talc, and alumina silicate, Alumina, oxidized silicon, magnesium oxide, zirconium oxide, titanium oxide, Carbonate, such as metallic compounds, such as iron oxide, calcium carbonate, magnesium carbonate, and dolomite, Sulfate, such as calcium sulfate and barium sulfate, magnesium hydroxide, Hydroxide, such as calcium hydroxide and aluminium hydroxide, a glass bead, It is also possible to blend non-fibrous

fillers, such as a ceramic bead, boron nitride, silicon carbide, and silica, these may be hollow and it is also possible to use together two or more kinds of these bulking agents further.

[0023] Although there is no restriction in particular in the preparing method of the thermoplastics product used by this invention, The method of supplying the mixture of a raw material to usually publicly known melting mixers, such as a monopodium or a biaxial extrusion machine, a Banbury mixer, a kneader, and a mixing roll, and kneading at the temperature of 180–450 **, etc. can be mentioned as an example. A method which restriction in particular does not have in the mixed sequence foreword of a raw material, either, and carries out melt kneading of all the raw materials by the method of the account of combination Gokami, Melt kneading of a part of raw materials may be carried out by the method of the account of combination Gokami, and which methods, such as the method of blending and carrying out melt kneading of the further remaining raw material or the method of using a side feeder for a part of raw materials during melt kneading with the extrusion machine of an after-combination monopodium or two axes, and mixing the remaining raw material, may be used. About a small-quantity additive component, after kneading and pelletizing other ingredients by the above-mentioned method etc., of course, it is also possible to add before shaping and to present shaping.

[0024] Things for which a Plastic solid is acquired with a publicly known molding method in some numbers, such as injection molding, extrusion molding, compression molding, blow forming, and injection compression molding, are possible for the charge of a shield material which covers the electromagnetic waves which consist of a thermoplastic resin composition used by this invention, and fabricating by injection molding especially is preferred.

[0025] The electro-magnetic interference sealed materials which consist of a thermoplastic resin composition obtained in this way are the features with bigger having high shield nature in a not less than 800-MHz field than a field with a frequency of less than 800 MHz of electromagnetic waves.

[0026] Using the device of the KEC method, the shield level of field intensity uses thickness as 1-mm tabular mold goods (let size of length and width be the predetermined size in a measuring device), and the electro-magnetic interference sealed materials of this invention are measured, and it is determined by the method with which it is expressed by a following formula (2). It installs and, specifically, asks for tabular mold goods with a thickness of 1 mm which consists of a charge of a shield material of this invention so that the source of electric field dispatch and the source of electric field reception may be intercepted. In many cases, in a field with a frequency of 800 MHz, the electro-magnetic interference sealed materials of this invention can decrease field intensity to less than -30dB, and can attain a level of -35 dB or less in a more desirable mode to it. If an electromagnetic wave shield level is smaller than the above-mentioned maximum, electromagnetic waves can fully be covered.

[0027]

Field intensity shield level (dB) = $20 \log (E_1/E_0)$ (2)

However, E_0 : The level (V/m) of the source of electric field reception when not placing a shield material

E_1 : The level (V/m) of the source of electric field reception at the time of placing a shield material.

[0028] The electro-magnetic interference sealed materials of this invention are suitably used as a Plastic solid of electromagnetic wave shield parts, such as the personal digital assistant with which we are anxious about malfunction of the apparatus by electromagnetic waves, or the adverse effect to a human body, electrical machinery electronic equipment, a household appliance article, a precision mechanical equipment, medical equipment, and electronic equipment for vehicles.

[0029]

[Example] An example is shown below and this invention is explained to it still more concretely. The flexural strength and the rate of bending flexibility which are described in an example and a comparative example were measured according to ASTM-D790. Electromagnetic wave shielding

measured the shielding characteristic of the electric field by the KEC method (MA8602B by ANRITSU CORP.).

[Reference example 1]

(Manufacture of PPS) To autoclave with an agitator, 4.67 kg (25 mol of specific hydrosulfides) of specific hydrosulfide solution, 2 kg (25 mol of sodium hydroxide) of sodium hydroxide and 8 kg of N-methyl-2-pyrrolidone (it omits the following NMP.) were taught 50%, temperature up was carried out gradually, agitating, and the distillate water 4.1L containing 3.8 kg of water was removed. 3.75 kg (25.5 mol) of 1,4-dichlorobenzene and NMP2kg were added to the remains mixture, and it heated at 230 ** for 1 hour. With warm water, the resultant was thrown in after 5 times washing and in 90 ** and the pH 4 acetic acid solution 25L, and was agitated for 1 hour. Polyphenylene sulfide resin was filtered, and after 90 ** ion exchange water washed until the pH of filtrate was set to seven, vacuum drying was carried out at 80 ** for 24 hours. After carbonizing a melt flow rate (MFR) at 870g / 10min, and 450-500 ** using a with 31.75 mm in length, and a diameter of 2.10 mm orifice when it measures by the temperature of 316 **, and 20 g of load, the amount of ash residues at the time of making it incinerate at 538 ** for 6 hours was 0.19 % of the weight.

[Reference example 2] (manufacture of a carbon nanotube) on the stick made from graphite the diameter of 7 mm, and 48 mm in length. Along with the medial axis, the with the diameter of 3 mm and a depth of 29 mm hole was made from the tip, the powder mixture of rhodium:platinum:graphite =5:5:2 was filled in this hole, and the anode for carbon nanotube manufacture was created. On the other hand, the negative pole the diameter of 14 mm and 31 mm in length which consists of graphite of purity 99.998% was created. These electrodes were installed into the vacuum chamber, the inside of a chamber was replaced by gaseous helium of 99.9% of purity, and DC arc discharge was performed. The interval of the anode and the negative pole was always controlled to 1-2 mm, and it discharged with pressure 600torr and the current 70A. The carbon nanotube generated on the negative pole was taken out. The carbon nanotube which consists of a graphite layer of a monolayer 5 nm in inside diameter, the outer diameter of 10 nm, and 1-10 micrometers in length and a double layer was obtained.

[The compounding agent used by the example and the comparative example]

PPS resin: -- PPS resinPBT resin: obtained with the manufacturing method of the above-mentioned reference example 1 -- "TOREKON"1401X31 (made by Toray Industries)

carbon nanotube: -- carbon nanotube conductive fiber: obtained with the manufacturing method of the above-mentioned reference example 2 -- carbon fiber -- "a trading card" -- a chopped strand (made by Toray Industries) T-300SC, the mean fiber diameter of 6 micrometers, and 10 mm in length

Glass fiber: A chopped strand TN717, the mean fiber diameter of 13 micrometers, and 10 mm in length (NEC glass).

[Examples 1-5 and comparative examples 1-8] Thermoplastics (PPS resin, PBT resin), After carrying out the dry blend of a carbon nanotube, carbon fiber, and the glass fiber at a rate shown in Table 1 and Table 2, when PPS resin was used and 320 ** and PBT resin were used, it pelletized after melt kneading with the biaxial screw-type extrusion machine set as 260 ** extrusion conditions. PPS resin obtained the predetermined specimen for characterization after drying the obtained pellet using the injection molding machine by carrying out injection molding of the cylinder temperature of 320 **, the die temperature of 130 **, and the PBT resin on with the cylinder temperature of 260 **, and a die temperature of 60 ** conditions. About each obtained specimen, the result of having measured flexural strength and the rate of bending flexibility is shown in Table 1 and Table 2. The electromagnetic wave shield level of the Plastic solid of the charge of a shield material by which injection molding might be carried out in the 150x150x1-mm thickness corner guard is shown in Table 1 and Table 2.

[0030]The result of having measured electromagnetic wave shielding by the KEC method is shown in drawing 1 - 3 about the charge of a shield material of Example 3 and the comparative examples 2

and 3. The result of having measured electromagnetic wave shielding like Example 3 and the comparative examples 2 and 3 about the Plastic solid which performed nickel and coppering to the 150x150x1-mm thickness corner guard made with ABS plastics ("TOYORAKKU" T-100) as reference is shown in drawing 4.

[0031]

[Table 1]

表 1

		実施例1	実施例2	実施例3	実施例4	実施例5
PPS樹脂		84	74	64	—	—
PBT樹脂		—	—	—	82	67
カーボンナノチューブ		6	6	6	3	3
炭素繊維		10	20	30	15	30
ガラス繊維		—	—	—	—	—
800MHz電磁波シールド性	(dB)	-36	-38	-41	-35	-38
曲げ強度	(MPa)	188	227	263	147	226
曲げ弾性率	(GPa)	6.5	17	22	8	17

[0032]

[Table 2]

表 2

		比較例1	比較例2	比較例3	比較例4	比較例5	比較例6	比較例7	比較例8
PPS樹脂		80	70	50	90	64	—	—	—
PBT樹脂		—	—	—	—	—	85	70	80
カーボンナノチューブ		—	—	—	10	6	15	30	40
炭素繊維		20	30	50	—	—	—	—	—
ガラス繊維		—	—	—	—	30	—	—	—
800MHz電磁波シールド性	(dB)	-18	-24	-26	-8	-7	-10	-18	-22
曲げ強度	(MPa)	225	260	280	160	205	150	230	252
曲げ弾性率	(GPa)	14	20	30	5	10	7	16	20

The electro-magnetic interference sealed materials which consist of a thermoplastic resin composition obtained in the example can be obtained on levels also with a high mechanical characteristic and electromagnetic wave shielding [with a frequency of not less than 800 MHz / enough / a mechanical characteristic] so that clearly from the result of Table 1. Like the result of the electromagnetic wave shielding frequency dependence of Example 3 shown in drawing 1, the electro-magnetic interference sealed materials which consist of a thermoplastic resin composition obtained in the example are the high frequency of not less than 800 MHz, and show the action electromagnetic wave shielding [whose] improves. This action is a phenomenon seen specifically, when a carbon nanotube and the carbon fiber which is conductive fibers are contained.

[0033] On the other hand, electromagnetic wave shield levels enough in the comparative examples 1-8 could not be obtained, but there was also much variation. Since it is necessary to perform plating treatment distance after performance degradation is seen and fabricates in a high frequency range although electromagnetic wave shielding [for ABS plastics / sufficient in the Plastic solid which performed nickel and coppering] is obtained, it is inferior to workability.

[0034]

[Effect of the Invention] The electro-magnetic interference sealed materials and the Plastic solid which consist of a thermoplastic resin composition of this invention have electromagnetic wave shielding [excellent in the frequency domain with a frequency of 800 MHz], and can prevent the obstacle by electromagnetic waves.

[Translation done.]